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## Different chromium content and thermal annealing influence on ions implanted Fe-Cr model alloys

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**Abstract**

Reduced activation ferritic/martensitic steels (RAFM) represented by binary Fe-Cr alloys, with different chromium content, were studied in as-received state as well as after helium ions implantation. In order to study changes in dependence on the temperature, thermal annealing of He ions implanted Fe-11.62%Cr specimens was performed. Measurements by Pulsed Low Energy Positron System (PLEPS) in Garching, Germany were performed afterwards. Annealing out of defects at lower temperatures was not significant as was expected and some uncertainties are present. Extensive decrease of positron lifetime of defects was observed in specimens annealed at temperature 600 °C.

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**1. Introduction**

Current nuclear power plants (NPP) require radiation, heat and mechanical resistance of their structural materials with ability to stay operational during NPP planned lifetime. Radiation damage much higher, than in current NPP, is expected in new generations of nuclear power plants, such as Generation IV and fusion reactors.

Investigation of structural materials is among others focused on study of reduced activation ferritic/martensitic (RAFM) steels with good characteristics as reduced activation, good resistance to volume swelling, good radiation, and heat resistance. From this point of view, these steels are considered for application in future fission and fusion reactors.

Our work is focused on study of radiation damage and thermal treatment evaluation of RAFM steels represented by binary Fe-Cr model alloys and partially on chromium influence on the increase of radiation damage resistance.

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For definite evaluation of chromium influence, model binary Fe-Cr alloys with varied chromium content and different damage levels were studied. Irradiation of structural materials is the main source of changes/damage in microstructure. Therefore, approach for restoration of initial physical and mechanical characteristics of structural materials was applied in form of thermal annealing with goal to eliminate size and amount of accumulated defects.

Experimental analysis of material damage on microstructural level was performed by non-destructive technique - positron annihilation spectroscopy (PAS), particularly by pulsed low energy positron system (PLEPS) with time resolution of ~260 ps (FWHM) and conventional positron annihilation lifetime spectroscopy (PALS) with time resolution of ~220 ps (FWHM) using  $^{22}\text{Na}$  source.

Application of PLEPS [1] at the high intensity positron source NEPOMUC [2, 3] at the Munich research reactor FRM-II gives us, in comparison with PALS, opportunity to investigate specific depths due to energy of positrons which can be set to specific levels (0.5 eV – 20 keV). It also allows investigation of near surface regions and provides information about defects in the structure, namely, their size and distribution.

Difficulties connected with experiments, performed under conditions actually present during reactor operation, led us to simulation of radiation damage by ion beams ( $\text{He}^+$  ions) at different levels reaching high fluencies expected in new reactor concepts. Implantation was performed by linear accelerator at Department of Nuclear Physics and Technology and the vacancy type defects produced by helium ions were studied in details.

## 2. Materials treatment

Detailed chemical composition of studied Fe-Cr alloys with different chromium content can be seen in the table 1. More information about fabrication processes and heat treatment of reduced activation ferritic/martensitic steels can be found in [4]. “As-received” materials were cut to desired dimensions (10x10x0.4 mm), ground and polished (grain size ~200 nm) to mirror-like surfaces before exposure to helium implantation. Subsequently, non-implanted reference specimens and the implanted specimens were investigated with positron annihilation techniques.

Table 1. Chemical composition of studied Fe-Cr alloys [4].

Alloy	Cr*	O*	N*	C*	Mn	P	Ni	Cu	V
L251	2.36	0.035	0.012	0.008	0.009	0.013	0.044	0.005	0.001
L259	4.62	0.066	0.013	0.02	0.02	0.011	0.06	0.01	0.001
L252	8.39	0.067	0.015	0.021	0.03	0.012	0.07	0.01	0.002
L253	11.62	0.031	0.024	0.028	0.03	0.05	0.09	0.01	0.002

\* *measured after heat treatment*

Accelerated helium ions were used to obtain cascade collisions in the microstructure of studied materials without neutron activation. Helium implantation was performed in two steps with ions energy 250keV and 100keV, respectively. Implantation at different dose levels (Tab.2) was performed at the linear accelerator of the Slovak University of Technology in Bratislava [5]. The ion energies were chosen to ensure possibility of application of non-destructive techniques, sensitive in near surface areas (PAS, SEM, etc.). Applicability of these energies was also simulated by SRIM code (Stopping and Range of Ions in Matter) [6].

Table 2. Implantation doses of 250 & 100 keV He of studied Fe-Cr alloys.

Cr content [%]	2.36		4.62		8.39		11.62			
Specimen	L25100	L25101	L25900	L25901	L25200	L25201	L25300	L25301	L25303	L25305
Dose	Ions/cm <sup>2</sup>	0	6.24x10 <sup>17</sup>	0	6.24x10 <sup>17</sup>	0	6.24x10 <sup>17</sup>	0	6.24x10 <sup>17</sup>	1.87x10 <sup>18</sup> 3.12x10 <sup>18</sup>
	C/cm <sup>2</sup>	0	0.1	0	0.1	0	0.1	0	0.1	0.3 0.5

Specimens were thermally treated after PLEPS measurement at different implantation doses with aim to understand influence of annealing on structure formation and defects behaviour. Thermal treatment was performed at „Universität des Bundeswehr“ in Neubiberg (Munich, Germany). Specimens of Fe-11.62%Cr were annealed in argon atmosphere (10 kPa) at temperatures of 400, 475, 525 and 600 °C for 2 hours, than gradually cooled down and repeatedly measured after each temperature by PLEPS technique.

### 3. Results

Depth profiling of vacancy type defects was performed by PLEPS on “as-received” Fe-11.62%Cr specimen and three Fe-11.62%Cr specimens with different damage levels (Tab.1.2) using positron implantation energies between 2 keV and 18 keV corresponding to the depth of 15 – 525 nm.

Evaluation of Fe-11.62%Cr measured spectra was performed by PosWin code [7, 8] and the spectra were decomposed into the three components assigned as,  $\tau_1$ - positron annihilation in bulk,  $\tau_2$ - positron annihilation in defects (vacancies, vacancy clusters) and  $\tau_3$ - positron annihilation in large defects (voids).

Interpretation of data achieved by PLEPS technique was significantly influenced by the Scanning Electron Microscopy (SEM) results performed at Institute of Materials Science (Faculty of Materials Science and Technology, STU). Diagonal cut under the 12° angle for SEM technique (Fig.1) was performed in specimen Fe-11.62%Cr implanted at level of 0.3 C/cm<sup>2</sup> and annealed at temperature of 475 °C.

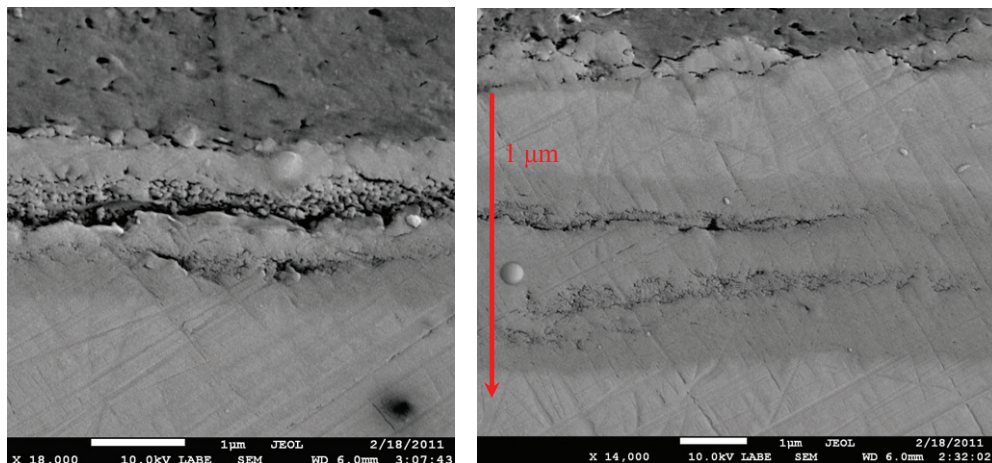


Figure 1. Alloy Fe-11.62%Cr annealed at 475 °C and implanted at 0.3 C/cm<sup>2</sup>.

The figure shows major damage in two regions. If we consider results achieved from Stopping and Range of Ions in Matter (SRIM) simulation (Fig.2), this two regions could be assigned to the maximum damage caused by He ions implantation. The first peak (Fig.2) in depth of ~300 nm is very significant and implies damage from 100 keV and partially also from 250 keV helium ions. This can be recognized also from the SEM figures, where the area closer to the surface has more significant damage (100 keV He) than the one further from the surface, influenced mainly by 250 keV He ions. SEM and SRIM results of maximum damage depth correlate well, but small deviations (50-100 nm) are present. This could be influenced by undulation on the surface of diagonal cut of the specimen.

According to [9], annealing at temperatures between 0.3T<sub>m</sub>-0.4T<sub>m</sub> (melting temperature ~ 1500 °C) can cause void and dislocation structure formation (the dislocation loops are unstable and grow into a dislocation networks) and diffusion is sufficient for the formation of precipitates. This corresponds well with annealing temperature of 475 °C, as ions damaged area was multiplied and voids reached its width of tens of nanometres.

Specimens implanted at level 0.3 and 0.5 C/cm<sup>2</sup> registered significant decrease of mean positron lifetime (MLT) at temperature of 600 °C (Fig.3). Analysis based on the MLT at this temperature could be interpreted as extensive decrease of defect size. Specimens irradiated at 0.3 and 0.5 C/cm<sup>2</sup> show growing MLT from the depth of ~170 nm to the surface. This growth of MLT could be assigned to the oxide layer on the surface. The minimum of the trend line is close to the area (depth) of large voids unrecognizable by positron techniques at annealing temperature of 475 °C. Then, the increase of MLT trend line from depth of ~ 300 nm is recognized and implanted 250 keV helium ions can participate on its increase. If we take into account complicated system as Fe-Cr alloys after all treatments, mean lifetimes can be in some way misleading. Therefore, the components of measured spectra also have to be analyzed for better understanding.

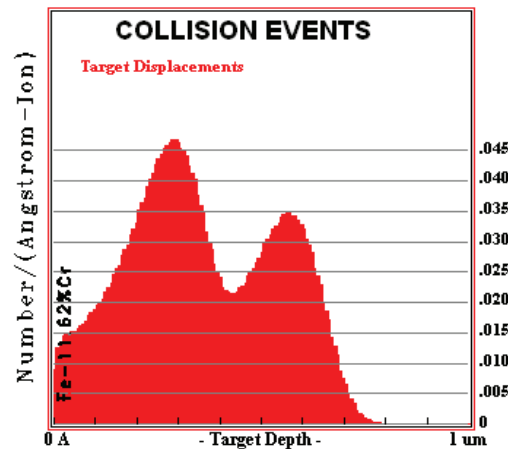


Figure 2. SRIM simulation of damage by 100keV (left peak) and 250keV (right peak) He ions.

Considering the theoretical statements from [9] for RAFM steels, comes to continuous annealing out of displacement damage above  $0.4T_m$ , resulting in little change in strength (at these temperatures strength sometimes decreases because irradiation-enhanced diffusion accelerates the normal thermal aging process). Therefore, we could say that such great voids in affected area were at temperature of 600 °C annealed out or at least their size decreased to small vacancy clusters.

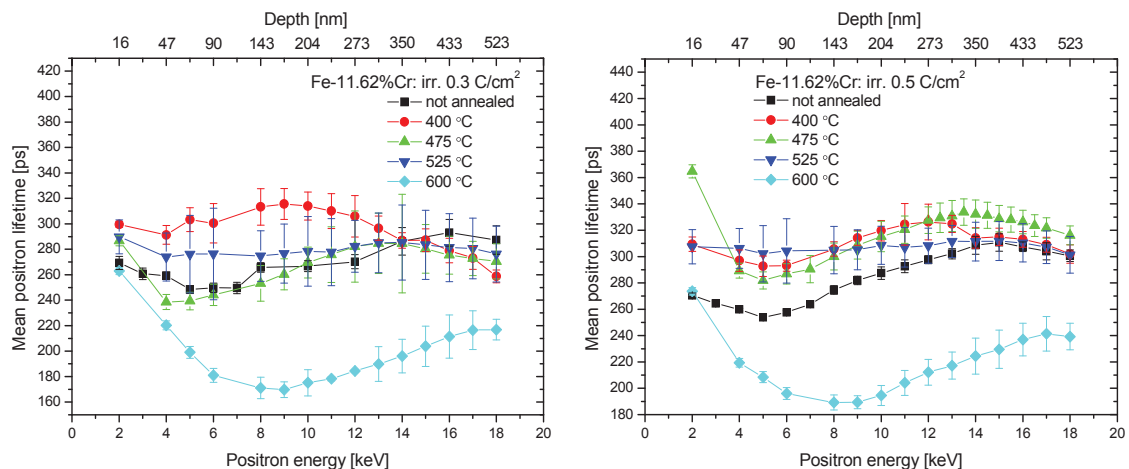


Figure 3. Mean positron lifetimes of Fe-11.62%Cr alloys.

### 3.1 Study of chromium influence

Specimens with different chromium content according to the table 2 were evaluated after 250 keV and 100 keV He ions implantation energies, respectively. This measurement was performed only at “as-received” specimens and at  $0.1 \text{ C/cm}^2$  implantation dose. According to figure 4, showing the results achieved by PALS (Positron annihilation lifetime spectroscopy), is mean positron lifetime (MLT) at level of  $\sim 148 \text{ ps}$  for “as-received” specimens and for dose of  $0.1 \text{ C/cm}^2$  is at level of about  $154 \text{ ps}$ . According to [10], these mean lifetimes characterize bulk with dislocations. Major changes in MLT values are not observed in dependency on different chromium content. This is much lower in comparison to results achieved by PLEPS (Fig.5) technique.

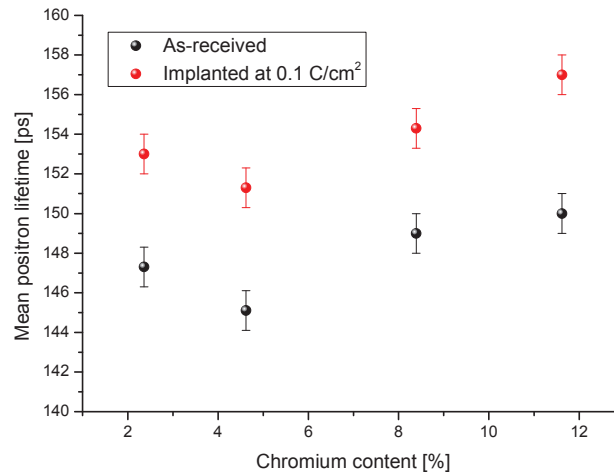


Figure 4. MLT of specimens with different chromium content by PALS.

MLT measured by PLEPS in 0.1 C/cm<sup>2</sup> implanted specimens with different chromium content reaches lowest values of ~ 230 ps and then goes higher. Difference between PALS and PLEPS results of MLT is from 60-130 ps. Such enormous growth of MLT can not be explained as errors of techniques and it has to be assigned to the ability of PLEPS technique to see increased amount of defects. According to [10], results would be achieved by PLEPS interpreted as significant presence of vacancy clusters. MLT increase in case of “as-received” specimens did not reach such variations as in case of implanted specimen probably due to the uninfluenced structure by ions implantation. Some defects can be present from the fabrication of alloys or caused by oxidation. With increasing content of chromium, mean lifetime slightly decreases and except of the Fe-2.36Cr alloys is the MLT at level of about 190 ps. This makes difference of about 20-40 ps in comparison to the PALS results. Mean lifetimes of implanted specimens were quite similar with respect to deviations but the lowest values were registered in Fe-11.62Cr specimen. Influence of the bulk structure on final PALS results could be also indirectly influenced by blistering due to the exposed undamaged structure (bulk).

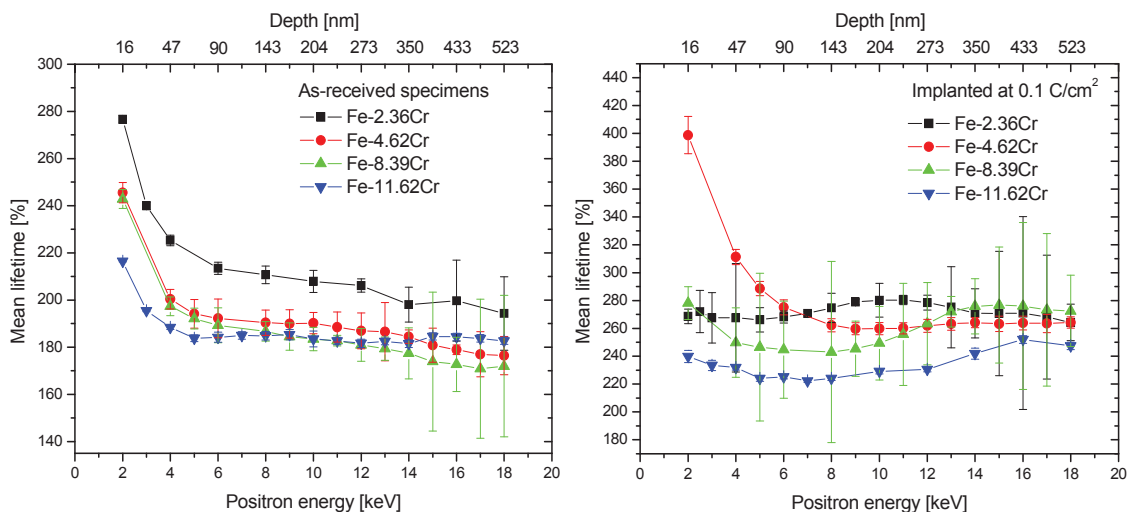


Figure 5. MLT of specimens with different chromium content by PLEPS.

#### 4. Conclusion

Investigation of Fe-Cr alloys with different chromium content and thermal annealing of chosen specimens were performed in this work. Evaluation of the measured data of annealed (475 °C) Fe-11.62%Cr alloys by PLEPS technique was significantly influenced by Scanning Electron Microscopy (SEM) results which showed major damage in two helium influenced regions. Expected damage in form of increased positron lifetimes was not observed in case of 600 °C annealing temperature and significant decrease of defects positron lifetimes from large voids to smaller vacancy clusters was well recognized. Considering the literature [9] about temperature influence on reduced activation ferritic/martensitic steels above  $0.4T_m$  (melting temperature), we could say that such great voids in affected area ( $<1\ \mu\text{m}$ ) were continuously annealed out or at least their size decreased to small vacancy clusters.

Influence of different chromium content in case of “as-received” and  $0.1\ \text{C}/\text{cm}^2$  implanted specimens was not so significant even though the MLT of ion implanted specimens increased. Difference of about 10 ps was recognized in PALS technique and also in PLEPS were small deviations between particular implantation doses. Significant chromium influence was very well recognized in our former experiments at higher implantation doses [11].

Ion implantation damage occurred in specimens was at very high level and with connection to the thermal annealing and oxide layer on the surface introduced many variables and created complicated system for the final evaluation of measured data. Even though the positron annihilation spectroscopy is very applicable technique for the vacancy type defects study, some limitations in form of inability to study specific depths (PALS) or defining too large defects (PLEPS) were recognized. Therefore, other destructive or non-destructive techniques have to be used to give us different point of view on examined materials.

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